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(54) COPPER FOIL FOR PRINTED CIRCUIT BOARD AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To improve adhesion strength to a substrate and to obtain good heat resistance and electric characteristics by forming a burnt copper plating layer containing Mo and at least one of Fe, Co, Ni and W on the surface of the adhering face of a source copper foil.

SOLUTION: In the production of a copper foil, a burnt plating layer of copper is formed on the surface of the copper foil by electrolysis using an acid copper electrolytic bath and the objective copper foil as the cathode at a current density near the limit current density of the bath. In this process, the electrolytic liquid of the bath preferably contains 0.001 to 5 g/l of Mo and at least one of Fe, Co and Ni and W by 0.01 to 10 g-M/l, in a soln. state, wherein M represents Fe and/or Co and/or Ni and/or W. As for the acid copper electrolytic bath, usually, a sulfuric acid bath (containing copper sulfate as copper) is preferably used. The burnt plating layer formed is preferably 0.2 to 2.5 μm thick.

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(54) 【発明の名称】 プリント配線板用銅箔及びその製造方法

(57) 【要約】

【課題】 基板への接着面表面が均質でムラがなく、粉落ちの点で問題がなく、基板との間で十分な接着強度を有し、耐熱性あるいは電気的特性においても優れたプリント配線板用銅箔及びその製造方法を提供する。

【解決手段】 プリント配線板用銅箔であって、原料銅箔の被接着面側表面に、モリブデンと、鉄、コバルト、ニッケル、タングステンの内の少なくとも1種と、を含有する銅のやけめっき層を有することを特徴とする。

【特許請求の範囲】

【請求項1】 原銅箔の被接着面側表面に、モリブデンと、鉄、コバルト、ニッケル、タングステンの内の少なくとも1種と、を含有する銅のやけめっき層を有することを特徴とするプリント配線板用銅箔。

【請求項2】 前記のやけめっき層の上に銅のめっき層を更に有する請求項1に記載の銅箔。

【請求項3】 前記の銅のやけめっき層又は銅のめっき層の上にニッケルめっき層又は亜鉛めっき層若しくはニッケルめっき層+亜鉛めっき層を更に有する請求項1又は2に記載の銅箔。

【請求項4】 前記の銅のめっき層又はニッケルめっき層、亜鉛めっき層若しくはニッケルめっき層+亜鉛めっき層の上にクロメート皮膜を更に有する請求項2又は3に記載の銅箔。

【請求項5】 前記のやけめっき層の厚みが0.2～5.0 μm である請求項1乃至4のいずれか1に記載の銅箔。

【請求項6】 酸性銅電解溶を用い、被処理銅箔を陰極とし、該溶の限界電流密度付近の電流密度で電解して該銅箔表面に銅のやけめっき層を形成するプリント配線板用銅箔の製造方法において、該溶の電解液中にモリブデンを0.001～5g-Mo/l、鉄、コバルト、ニッケル、タングステンの少なくとも1種を0.01～10g-M/l ($M = \text{Fe}$ 及び/又は Co 及び/又は Ni 及び/又は M)、溶液の形態にて含有することを特徴とする方法。

【請求項7】 前記のやけめっき層を形成する工程に次いで、該やけめっき層の上に銅のめっき層を形成する工程を行う請求項6に記載の方法。

【請求項8】 前記のやけめっき層を形成する工程又は銅のめっき層を形成する工程に次いで、該銅のやけめっき層又は該銅のめっき層の上にニッケルめっき層又は亜鉛めっき層若しくはニッケルめっき層+亜鉛めっき層を形成する工程を行う請求項6又は7に記載の方法。

【請求項9】 前記の銅のめっき層又はニッケルめっき層、亜鉛めっき層若しくはニッケルめっき層+亜鉛めっき層を形成する工程に次いで、該銅のめっき層又はニッケルめっき層、亜鉛めっき層若しくはニッケルめっき層+亜鉛めっき層の上にクロメート皮膜を形成する工程を行う請求項7又は8に記載の方法。

【請求項10】 前記の電解溶が硫酸銅-硫酸浴である請求項6乃至9のいずれか1に記載の方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、プリント配線板用銅箔及びその製造方法に関する。

【0002】

【従来の技術】 プリント配線板用銅箔は、それを基材に接合させるにあたり、その、接着強度を向上させ、プリント配線板としての所要の電気特性、エッチング特性、

耐熱性、耐薬品性を満足させるために、該銅箔の被接合面に粗化処理を施し、更には該粗化処理を施された面上に亜鉛めっきやニッケルめっき等を施し、また更には該亜鉛めっきやニッケルめっき等を施された面上にクロメート処理等を施す等、種々工夫されている。

【0003】 最近多用されているそれらの具体的方法としては、下記のもの挙げられる。

【0004】 ① 特公昭40-15327号に開示された方法

酸性銅電解溶中で銅箔を陰極とし、限界電流密度付近で電解を行うことにより、いわゆる「やけめっき」を施して粗化面を得る方法である。

【0005】 ② 米国特許第3293109号に開示された方法

「やけめっき」を施された粗化面の微細な突起群の表面を通常の銅めっきの薄層（いわゆる「カプセル層」）で覆って、該粗化面の微細な突起群を銅箔の安定的に固定する方法。

【0006】 ③ 特公昭54-38053号に開示された方法

比較的大きな樹枝状突起の生成を防止し、より微細で且つ全面が均一な突起群よりなる粗化面を得るために、酸性銅電解溶の電解液中にセレン、テルル、ヒ素、アンチモン、ビスマスの少なくとも1種を0.01～1g-M/l ($M = \text{Se}, \text{Te}, \text{As}, \text{Sb}, \text{Bi}$)に添加する方法。

【0007】 ④ 特公昭53-39327号に開示された方法

セレン、テルル、ヒ素、アンチモン、ビスマスの少なくとも1種を0.03～5g-M/l ($M = \text{Se}, \text{Te}, \text{As}, \text{Sb}, \text{Bi}$)に添加した電解液を含む酸性銅電解溶にて「やけめっき」を施し、形成された微細な樹枝状突起群の表面を通常の銅めっきの薄層で覆って該突起群の脱落を防止し粉状移着特性を改善すると共に基材に対する接着強度を改善せんとした方法。

【0008】 しかしながら、セレン、テルル、ヒ素、アンチモン、ビスマスを含む化合物は、毒物、劇物、もしくはこれらに類するものとされているものが多く、電解時にこれらの元素が銅電着物中に取り込まれる結果、銅箔やそれを用いたプリント配線板の再生時や廃棄時、またこれらの元素を含有することになるエッチング廃液の処分時に、環境への汚染に対し最大限の注意が必要である。更に、毒性の弱いものは、これらの元素を添加することによって得られる効果が小さい。

【0009】 一方、その中にこれらの金属を含まない電解液を用いたもの、すなわち銅のみの「やけめっき層」を形成したものは、たとえ「やけめっき層」の上に更に通常の銅めっき層を形成したとしても「やけめっき層」の微細突起自体が粗雑なものとなり、また該微細突起群は不均一である。このような「やけめっき層」を有する銅箔の被接着面の表面を摩擦するとかなりの量の微細銅

粉が剥落し、また樹脂基板と重ねて銅貼り積層板としたものはエッチングを行った後該基板表面に銅粉が残留する等の欠点を有していた。

【0010】これらの欠点を改良するものとして、a. ベンゾキノリン類を添加した電解液を用いて粗化处理を行う方法（特公昭56-44196号公報）；b. モリブデン及び／又はバナジウムを添加した電解液を用いて粗化处理を行う方法（特公昭62-56677号公報）；c. パルス電流を粗化处理のための電解液に供給する方法（特開昭58-16479号公報や特開昭63-17597号公報）；が提唱されているが、いずれの方法も前記の毒性の強い元素の化合物を含む電解液を用いた粗化处理にて得られる銅箔に比し、剥離強度、粉落ち等の点で劣るものしか得られなかった。

【0011】

【発明が解決しようとする課題】本発明は、従来の技術の課題を解決するためになされたものであって、基板への接着面表面が均質でムラがなく、粉落ちの点で問題がなく、基板との間で充分な接着強度を有し、耐熱性あるいは電気特性においても優れたプリント配線板用銅箔及びその製造方法を提供することを目的とする。

【0012】

【課題を解決するための手段】本発明は、プリント配線板用銅箔であって、厚銅箔の被接着面側表面に、モリブデンと、鉄、コバルト、ニッケル、タングステンの内の少なくとも1種と、を含有する銅の「やけめっき層」を有することを特徴とする。

【0013】ここで、前記の「やけめっき層」の膜厚（見かけ膜厚）は、0.2～2.5μmであることが好ましく、0.4～1.5μmであることが更に好ましい。ここで、「見かけ膜厚」とは、「やけめっき」の処理電流を流した時に電析する粒状のめっきを平滑めっきに換算して求めた膜厚である。

【0014】本発明の銅箔は、前記の「やけめっき層」の上に「銅のめっき層」（いわゆる「カプセル層」）を更に有するものであってもよい。

【0015】ここで、前記の「カプセル層」の膜厚（見かけ膜厚）は、0.2～2.5μmであることが好ましく、0.4～1.5μmであることが更に好ましい。

【0016】尚、本発明の銅箔は、所望により、更に前記の「やけめっき層」又は「カプセル層」の上に「ニッケルめっき層」又は「亜鉛めっき層」若しくは「ニッケルめっき層」＋「亜鉛めっき層」を形成せしめたものであってもよいし、又さらにはこれら「カプセル層」又は「ニッケルめっき層」、「亜鉛めっき層」若しくは「ニッケルめっき層」＋「亜鉛めっき層」の上にクロメート皮膜を形成せしめたものであってもよい。

【0017】一方、本発明の銅箔の製造方法は、酸性銅電解液を用い、被処理銅箔を陰極とし、該浴の限界電流密度付近の電流密度で電解して該銅箔表面に銅の「やけ

めっき層」を形成するプリント配線板用銅箔の製造方法であって、該浴の電解液中にモリブデンを0.001～5g-Mo/l、鉄、コバルト、ニッケル、タングステンの少なくとも1種を0.01～10g-M/l（M = Fe及び／又はCo及び／又はNi及び／又はW）、溶液の形態にて含有することを特徴とする。

【0018】ここで、モリブデン濃度が0.001g-Mo/l未満では所望の効果が顕著ではないし、一方5g-Mo/l超でも所望の効果がその存在量の増加に比し顕著に増大しないので経済的ではなく、更に「やけめっき層」が粉状化しやすくなるので好ましくない。鉄、コバルト、ニッケル、タングステンの規定濃度外の挙動もモリブデンのそれと同様である。尚、これらの添加剤の形態は電解液に溶解するものであれば特に限定されない（ただし、これらのハロゲン化合物も殆どのものが電解液に溶解するが、粗化处理に悪影響を及ぼすので好ましくない）が、代表的な化合物としては下記のもの挙げられる。

1. モリブデン : モリブデン酸ナトリウム（2水塩）
2. 鉄 : 硫酸第1鉄（7水塩）
3. コバルト : 硫酸コバルト（7水塩）
4. ニッケル : 硫酸ニッケル（7水塩）
5. タングステン : タングステン酸ナトリウム（2水塩）

【0019】酸性銅電解液としては、鉍酸であればいずれの酸でも使用し得るが、通常は、硫酸浴（銅として硫酸銅含有）を用いる。

【0020】硫酸銅－硫酸浴の液組成、液温は広い範囲で選択可能であるが、それらによって浴の限界電流密度はそれぞれの値を示すので、使用する電流密度は、液組成や液温、さらには液の動きなどで異なり、また「やけめっき」だけを施すのか、それとも更にその上に通常の銅めっき又は亜鉛めっき若しくはニッケルめっき等をカプセル上に施すのか、によっても異なるため、多少、電流密度を加減する必要がある。

【0021】工業的にもちいられるのに好適な酸性銅電解液の液条件を例示すると下記の通りである。

1. 銅 : 5～50g-Cu/l
2. モリブデン : 0.001～5g-Mo/l
3. その他 : 0.01～10g-M/l（M = Fe, Co, Ni or Wの一種以上）
4. 酸 : 10～100g-H₂SO₄/l
5. 液温 : 室温～50℃

【0022】更に、浴の循環量も特に限定されないが、浴成分の消耗分を補給する程度を下限とし、陰極表面近傍領域が著しい乱流域とならぬ程度を上限とし、その間で適宜選択するのが好ましい。

【0023】また、処理時間は、数秒乃至数十秒の範囲が实际的で好ましいので、この程度の時間で所望の微細突起群が完成するよう、液組成や電流密度等の操作条件を設定するのがよい。

【0024】本発明の銅箔の製造方法においては、前記の「やけめっき層」を形成する工程に次いで、該「やけめっき層」の上に「銅のめっき層」又は「ニッケルめっき層」、「亜鉛めっき層」若しくは「ニッケルめっき層」+「亜鉛めっき層」を形成する工程を行ってもよいし、所望により、更に該「銅のめっき層」形成工程に次いで、該「銅のめっき層」の上に「ニッケルめっき層」又は「亜鉛めっき層」若しくは「ニッケルめっき層」+「亜鉛めっき層」を形成する工程を行ってもよいし、更にまた該「銅のめっき層」形成工程又は該「ニッケルめっき層」形成工程、「亜鉛めっき層」形成工程若しくは「ニッケルめっき層」+「亜鉛めっき層」形成工程に次いで、該「銅のめっき層」又は該「ニッケルめっき層」、「亜鉛めっき層」若しくは「ニッケルめっき層」+「亜鉛めっき層」の上にクロメート皮膜を形成する工程を行ってもよい。これら追加工程の条件は、公知の方法のそれに従えばよい。

【0025】尚、本発明の製造方法における被処理銅箔は、電解銅箔であってもよいし、また圧延銅箔であってもよい。本発明の方法では、銅箔の種類を選ばないからである。

【0026】

【発明の実施の形態】以下に、本発明を実施例に基づいて更に詳しく説明する。但し、本発明はこれらに限定されるものではない。

【0027】実施例1

(1) 被処理銅箔（原銅箔）

電解銅箔（未処理銅箔）：厚さ：18 μ m；マツト面の粗さ： $R_a=0.6\mu$ m； $R_z=4.2\mu$ m；古河サニキットフイル（株）製

(2) やけめっき層の形成

原銅箔に下記の条件にて直流による陰極電解処理を施し、該原銅箔のマツト面上に微細な突起群からなる「やけめっき層」を電析させた。

① 電解液の組成

- ・硫酸銅 : 100g-CuSO₄·5H₂O/l
- ・硫酸 : 120g-H₂SO₄/l
- ・モリブデン : 0.6g-Na₂MoO₄·2H₂O/l
- ・鉄 : 15g-FeSO₄·7H₂O/l

② 電解液の温度 : 35℃

③ 電流密度 : 40A/dm²

④ 処理時間 : 3.5sec.

(3) カプセルめっき

マツト面上に微細な突起群が形成された前記の原銅箔に下記の条件にて直流による陰極電解処理を施し、該微細な突起群を銅の薄層で覆った。

① 電解液の組成

- ・硫酸銅 : 250g-CuSO₄·5H₂O/l
- ・硫酸 : 100g-H₂SO₄/l

② 電解液の温度 : 50℃

③ 電流密度 : 20A/dm²

④ 処理時間 : 7.0sec.

(4) 更に前記の(2)→(3)の処理をもう一度繰り返した。

(5) 表面処理

得られた銅箔（以下、「粗化処理銅箔」という）の被接合面側の表面に、ニッケル-リンめっき（0.1mg/dm²）と亜鉛めっき（0.1mg/dm²）を施し、更にその上にクロメート処理を施した試料（以下、「表面処理銅箔」という）を作成した。

【0028】得られた表面処理銅箔の特性を下記の項目についてそれぞれ評価した。

【0029】(1) ビール強度

得られた表面処理銅箔をFR-4基材にプレスし接着したものを試料とし、JIS C 6481「プリント配線板用銅箔積層板試験方法」の5.7に従って常態ビール（常態での「引きはがし強さ」）を測定した。

【0030】(2) 耐塩酸劣化率

得られた表面処理銅箔をFR-4基材にプレスし接着した後、該表面処理銅箔を1mm幅にエッチングしたものを試料とし、JIS C 6481「プリント配線板用銅箔積層板試験方法」の5.7に従って常態ビールと劣化処理後のビール（35%塩酸と蒸留水を同量混合した25℃の処理液に該試料を1時間浸漬したものの「引きはがし強さ」。以下、「劣化後ビール」という）を測定し、下記の式に従って計算にて求めた。

耐塩酸劣化率(%) = (1 - (劣化後ビール/常態ビール)) × 100

【0031】(3) 粉落ち

得られた表面処理銅箔上に試験紙（東洋ろ紙No. 2）を置き、それに荷重（250g/20mmφ）をかけたまま該試験紙を150mm水平方向に引きずった。該試験紙に付着する銅粉を目視観察し、付着量に応じてA<B<C<D<E<Fの順に評価付けした（A：粉落ち「ゼロ」、F：粉落ちが最も多い）。

【0032】結果を表1に示す。

【0033】実施例2

処理(2)における電解液の組成を下記のものに代えたことを除き実施例1と同様にして粗化処理銅箔及び表面処理銅箔をそれぞれ作製し、該表面処理銅箔について実施例1と同様の特性評価を行った。結果を表1に示す。

① 電解液の組成

- ・硫酸銅 : 100g-CuSO₄·5H₂O/l
- ・硫酸 : 120g-H₂SO₄/l
- ・モリブデン : 0.05g-Na₂MoO₄·2H₂O/l
- ・タングステン : 0.05g-Na₂WO₄·2H₂O/l

【0034】実施例3

処理(2)における電解液の組成を下記のものに代えたことを除き実施例1と同様にして粗化処理銅箔及び表面

処理銅箔をそれぞれ作製し、該表面処理銅箔について実施例 1 と同様の特性評価を行った。結果を表 1 に示す。

① 電解液の組成

- ・硫酸銅 : 100g-CuSO₄·5H₂O/l
- ・硫酸 : 120g-H₂SO₄/l
- ・モリブデン : 0.6g-Na₂MoO₄·2H₂O/l
- ・鉄 : 15g-FeSO₄·7H₂O/l
- ・タングステン : 0.03g-Na₂WO₄·2H₂O/l

【0035】実施例 4

処理 (2) における電解液の組成を下記のものに代えたことを除き実施例 1 と同様にして粗化処理銅箔及び表面処理銅箔をそれぞれ作製し、該表面処理銅箔について実施例 1 と同様の特性評価を行った。結果を表 1 に示す。

① 電解液の組成

- ・硫酸銅 : 100g-CuSO₄·5H₂O/l
- ・硫酸 : 120g-H₂SO₄/l
- ・モリブデン : 0.6g-Na₂MoO₄·2H₂O/l
- ・コバルト : 10g-CoSO₄·7H₂O/l

【0036】実施例 5

処理 (2) における電解液の組成を下記のものに代えたことを除き実施例 1 と同様にして粗化処理銅箔及び表面処理銅箔をそれぞれ作製し、該表面処理銅箔について実施例 1 と同様の特性評価を行った。結果を表 1 に示す。

① 電解液の組成

- ・硫酸銅 : 100g-CuSO₄·5H₂O/l
- ・硫酸 : 120g-H₂SO₄/l
- ・モリブデン : 0.6g-Na₂MoO₄·2H₂O/l
- ・ニッケル : 10g-NiSO₄·7H₂O/l

【0037】比較例 1

処理 (2) における電解液の組成を下記のものに代えたことを除き実施例 1 と同様にして粗化処理銅箔及び表面処理銅箔をそれぞれ作製し、該表面処理銅箔について実施例 1 と同様の特性評価を行った。結果を表 1 に示す。

① 電解液の組成

- ・硫酸銅 : 100g-CuSO₄·5H₂O/l
- ・硫酸 : 120g-H₂SO₄/l
- ・ヒ素 : 0.4cc/l as 60% H₃AsO₄ (比重: 1.58)

【0038】比較例 2

処理 (2) における電解液の組成を下記のものに代えたことを除き実施例 1 と同様にして粗化処理銅箔及び表面

処理銅箔をそれぞれ作製し、該表面処理銅箔について実施例 1 と同様の特性評価を行った。結果を表 1 に示す。

① 電解液の組成

- ・硫酸銅 : 100g-CuSO₄·5H₂O/l
- ・硫酸 : 120g-H₂SO₄/l
- ・モリブデン : 0.6g-Na₂MoO₄·2H₂O/l

【0039】実施例 1～5 及び比較例 1～2 にて得られた各粗化処理銅箔の粗化処理を施した面を硫酸-過酸化水素のソフトエッチング液 (H₂SO₄: 100g/l、H₂O₂: 30g/l、n-プロパノール: 10cc/l) に 1 分間浸漬して該粗化処理被膜を溶解し、該溶解液を蒸発乾固して該溶解液中に含まれる過酸化水素を分解除去した後、原子吸光分析法 (日立 (株) Z-6100 形偏光ゼーマン原子吸光分光光度計を使用) にて該溶解液中の対象元素の定量分析を行った。その結果を表 2 に示す。尚、データは該粗化処理被膜中の存在量に換算したものである。

【0040】

【表 1】

表 1

	やけめつき層中含 有金属 ^{*1}	ピール強 度 ^{*2} (kg/cm)	耐塩酸劣 化率 ^{*3} (%)	粉落ち ^{*4}
実施例 1	Mo, Fe	1.42	0	A
実施例 2	Mo, W	1.46	0	A
実施例 3	Mo, Fe, W	1.46	0	A
実施例 4	Mo, Co	1.43	2	C
実施例 5	Mo, Ni	1.42	2	C
比較例 1	As	1.46	0	B
比較例 2	Mo	1.28	2	E

【備考】

*1 銅を除く。

*2 常態ピールである。

*3 劣化率 = (1 - (常態ピール / 劣化後ピール)) × 100

*4 目視観察結果である。

【0041】

【表 2】

表 2

	表面処理被膜中の存在量 (ng/dm ²)					
	Mo	Fe	Co	Ni	W	As
実施例 1	0.020	0.005	-	-	-	-
実施例 2	0.002	-	-	-	0.002	-
実施例 3	0.013	0.002	-	-	0.001	-
実施例 4	0.011	-	0.002	-	-	-
実施例 5	0.008	-	-	0.002	-	-
比較例 1	-	-	-	-	-	0.172
比較例 2	0.021	-	-	-	-	-

【備考】分析された元素は主体としての銅を除くものである。

【0042】

【発明の効果】表 1 に示す通り、本発明の銅箔は、ピール強度、耐塩酸劣化率、粉落ち共毒性の強いヒ素を用いたもの（従来技術の一つ）と遜色ない性能を有するものである。これに対し、従来技術の他例（毒物を含まない）として挙げたモリブデン単用の銅箔は、ピール強度

が低く、粉落ちも多く実用上問題の大きいものであることがわかる。すなわち本発明に従えば、プリント配線板用銅箔としての所定の性能を十分に満足する環境に優しい銅箔及びそのための製造方法を提供することができる。

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CLAIMS

[Claim(s)]

[Claim 1] Copper foil for printed wired boards characterized by having the desperation plating layer of the copper containing molybdenum and at least one sort in iron, cobalt, nickel, and a tungsten at the pasted up field side front face of original copper foil.

[Claim 2] Copper foil according to claim 1 which has a copper plating layer further on the aforementioned desperation plating layer.

[Claim 3] Copper foil according to claim 1 or 2 which has further a nickel-plating layer, a galvanization layer, or a nickel-plating layer + galvanization layer on the desperation plating layer of the aforementioned copper, or a copper plating layer.

[Claim 4] Copper foil according to claim 2 or 3 which has a chromate film further on the plating layer of the aforementioned copper or a nickel-plating layer, a galvanization layer, or a nickel-plating layer + galvanization layer.

[Claim 5] the thickness of the aforementioned desperation plating layer -- 0.2-5.0 micrometers it is -- claim 1 thru/or copper foil given in any 1 of 4.

[Claim 6] In the manufacture approach of the copper foil for printed wired boards which uses processed copper foil as cathode, electrolyzes with the current density near the limiting current density of this bath using an acid copper electrolytic bath, and forms a copper desperation plating layer in this copper foil front face The approach characterized by containing at least one sort of 0.001-5g-Mo/l, iron, cobalt, nickel, and a tungsten for molybdenum in the electrolytic solution of this bath with the gestalt of 0.01 - 10 g-M/l (M = Fe, Co, nickel, and/or W) and a solution.

[Claim 7] The method according to claim 6 of subsequently to this desperation plating layer top carrying out the process which forms a copper plating layer to the process which forms the aforementioned desperation plating layer.

[Claim 8] The method according to claim 6 or 7 of subsequently to the desperation plating layer [of this copper], or plating layer top of this copper carrying out the process which forms a nickel-plating layer, a galvanization layer, or a nickel-plating layer + galvanization layer to the process which forms the plating layer of the process or copper which forms the aforementioned desperation plating layer.

[Claim 9] The method according to claim 7 or 8 of subsequently to a plating layer [of this copper] or nickel-plating layer, galvanization layer, or nickel-plating layer + galvanization layer top carrying out the process which forms a chromate film to the process which forms the plating layer of the aforementioned copper or a nickel-plating layer, a galvanization layer, or a nickel-plating layer + galvanization layer.

[Claim 10] Claim 6 whose aforementioned electrolytic bath is a copper-sulfate-sulfuric-acid bath thru/or an approach given in any 1 of 9.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the copper foil for printed wired boards, and its manufacture approach.

[0002]

[Description of the Prior Art] In joining it to a base material, since the copper foil for printed wired boards raises the bond strength and satisfies the necessary electrical property as a printed wired board, an etching property, thermal resistance, and chemical resistance Performing chromate treatment etc. on the field to which a galvanization, nickel plating, etc. were performed on the field to which roughening processing was performed to the plane of composition-ed of this copper foil, and this roughening processing was performed further, and also this galvanization, nickel plating, etc. were performed etc. is devised variously.

[0003] The following are mentioned as those concrete approaches used abundantly recently.

[0004] ** It is the approach of performing the so-called "desperation plating" and acquiring a roughening side, by using copper foil as cathode in the approach acidity copper electrolytic bath indicated by JP,40-15327,B, and electrolyzing near limiting current density.

[0005] ** How to cover the front face of the detailed projection group of a roughening side to which the approach "desperation plating" indicated by U.S. Pat. No. 3293109 was given by the thin layer (the so-called "capsule layer") of the usual copper plating, and fix the detailed projection group of this roughening side stably [copper foil].

[0006] ** How to add at least one sort of a selenium, a tellurium, an arsenic, antimony, and a bismuth in the electrolytic solution of an acid copper electrolytic bath at 0.01 - 1 g-M/l (M = Se, Te, As, Sb, Bi), in order to acquire the roughening side which was indicated by JP,54-38053,B and which prevents generation of a big and rough approach comparison arborescence projection, and consists of a more detailed projection group with the uniform whole surface.

[0007] ** The approach selenium, tellurium which were indicated by JP,53-39327,B, It is at least one sort of an arsenic, antimony, and a bismuth 0.03 - 5 g-M/l "Desperation plating" is performed with the acid copper electrolytic bath containing the electrolytic solution added (M = Se, Te, As, Sb, Bi). The approach which is going to improve the bond strength to a base material while covering the front face of the formed detailed arborescence projection group by the thin layer of the usual copper plating, preventing omission of this projection group and having improved the powder transfer property.

[0008] However, the compound containing a selenium, a tellurium, an arsenic, antimony, and a bismuth has many poison, deleterious substances, or things similar to these, and as a result of incorporating these elements in a copper electrodeposition object at the time of electrolysis, the maximum cautions are required for it at copper foil or the time of playback of the printed wired board using it, abandonment, and disposal of the etching waste fluid which will contain these elements to the contamination to an environment. Furthermore, a toxic weak thing has the small effectiveness acquired by adding these elements.

[0009] On the other hand, even if the thing using the electrolytic solution which does not contain these metals in it, i.e., the thing in which the copper "desperation plating layer" was formed, forms the further usual copper-plating layer on a "desperation plating layer", it will turn into what has the coarse detailed projection of a "desperation plating layer" itself, and this detailed projection group is uneven. What the detailed copper powder of the amount which rubs the front face of the pasted up field of the copper foil which has such a "desperation plating layer", or becomes exfoliated, and was made into copper-clad ***** in piles with the resin substrate had the fault of copper powder remaining on this substrate front face, after etching.

[0010] As what improves these faults a. benzoquinolines The added electrolytic solution It uses. Roughening processing How to perform ;b. molybdenum (JP,56-44196,B) And/or, although approach (JP,58-16479,A and JP,63-17597,A); which supplies the approach (JP,62-56677,B);c. pulse current which performs roughening processing using the electrolytic solution which added vanadium to the electrolytic bath for roughening processing is advocated It compared with the copper foil obtained by the roughening processing using the electrolytic solution with which any approach contains the compound of the strong aforementioned toxic element, and only what is inferior in respect of peel strength, powder omission, etc. was obtained.

[0011]

[Problem(s) to be Solved by the Invention] This invention is made in order to solve the technical problem of a Prior art, its adhesion side front face to a substrate is homogeneous, it does not have nonuniformity, is satisfactory in respect of powder omission, has bond strength sufficient between substrates, and aims at offering the copper foil for printed wired boards which was excellent also in thermal resistance or an electrical property, and its manufacture approach.

[0012]

[Means for Solving the Problem] This invention is copper foil for printed wired boards, and is characterized by having the "desperation plating layer" of the copper which contains molybdenum and at least one sort in iron, cobalt, nickel, and a tungsten on the pasted up field side front face of original copper foil.

[0013] here -- the thickness (appearance thickness) of the aforementioned "desperation plating layer" -- 0.2-2.5 micrometers it is -- things -- desirable -- 0.4-1.5 micrometers it is -- things are still more desirable. Here, "appearance thickness" is the thickness which converted into smooth plating the granular plating which carries out electrocrystallization, and asked for it, when the processing current of "desperation plating" is passed.

[0014] The copper foil of this invention may have further "a copper plating layer" (the so-called "capsule layer") on the aforementioned "desperation plating layer."

[0015] the thickness (appearance thickness) of the aforementioned "capsule layer" is 0.2-2.5 micrometers here -- desirable -- 0.4-1.5 micrometers it is -- things are still more desirable.

[0016] In addition, the copper foil of this invention may make "nickel-plating layer", "galvanization layer", or "nickel-plating layer" + "a galvanization layer" form on the further aforementioned "desperation plating layer" or a "capsule layer", and also may make a chromate film form by request on these "capsule layer" or "nickel-plating layer", "galvanization layer", or "nickel-plating layer" + "a galvanization layer."

[0017] On the other hand, the manufacture approach of the copper foil of this invention uses processed copper foil as cathode using an acid copper electrolytic bath. It is the manufacture approach of the copper foil for printed wired boards which electrolyzes with the current density near the limiting current density of this bath, and forms copper "desperation plating layer" in this copper foil front face. It is characterized by containing at least one sort of 0.001 - 5 g-Mo/l, iron, cobalt, nickel, and a tungsten for molybdenum in the electrolytic solution of this bath with the gestalt of 0.01 - 10 g-M/l (M = Fe, Co, nickel, and/or W) and a solution.

[0018] Since the effectiveness of a request of molybdenum concentration in less than 0.001 g-Mo/l is not remarkable here, and it further becomes easy for a "desperation plating layer" to disintegrate rather than economical since desired effectiveness also compares 5 g-Mo/l super-** with the increment in the

abundance and it does not increase notably on the other hand, it is not desirable. The behavior besides the normality of iron, cobalt, nickel, and a tungsten is the same as that of it of molybdenum. in addition, the gestalt of these additives will be limited especially if it dissolves in the electrolytic solution -- not having (however, it not being desirable since it has a bad influence on roughening processing although almost all things also dissolve these halogenides in the electrolytic solution) -- the following are mentioned as a typical compound.

1. Molybdenum : Sodium Molybdate (Two Monohydrates)
2. Iron : Ferrous Sulfate (Seven Monohydrates)
3. Cobalt : Cobalt Sulfate (Seven Monohydrates)
4. Nickel : Nickel Sulfate (Seven Monohydrates)
5. Tungsten : Sodium Tungstate (Two Monohydrates)

[0019] Although any acid can be used as an acid copper electrolytic bath if it is a mineral acid, a sulfuric-acid bath (copper-sulfate content as copper) is usually used.

[0020] Although the liquid presentation of a copper-sulfate-sulfuric-acid bath and solution temperature are selectable in the large range Since the limiting current density of a bath shows each value by them, the current density to be used a liquid presentation, solution temperature, and differing by motion of liquid etc. further and performing "desperation plating" -- or since it differs "boil whether copper plating, a usual galvanization, or usual nickel plating etc. is further performed on a capsule on it", it is necessary to adjust current density somewhat

[0021] It is as follows, when it has industrially and the liquid conditions of an acid suitable copper electrolytic bath to be are illustrated.

1. Copper : 50 [5 -] G-Cu/l2. Molybdenum: 0.001 - 5 G-Mo/l3., Others : 0.01 - 10 G-M/l (More Than a Kind of M = Fe, Co, and Nickel or W)

4. Acid : 10 - 100 G-H₂SO₄/L5. Solution Temperature : Room Temperature -50 Degree-C[0022]

Furthermore, although especially the circulating load of a bath is not limited, either, it is desirable to make into a minimum extent which supplies an exhausted part of a bath component, to make into an upper limit extent from which the field near the cathode surface does not turn into a remarkable turbulent flow region, and to choose suitably by the meantime.

[0023] Moreover, since the processing time is desirable, it is good [the processing time / its range for several seconds thru/or dozens of seconds is practical, and] to set up operating conditions, such as a liquid presentation and current density, so that a desired detailed projection group may be completed by time amount of this level.

[0024] In the manufacture approach of the copper foil of this invention, at the process which forms the aforementioned "desperation plating layer", subsequently May perform the process which forms "copper plating layer" or "nickel-plating layer", "galvanization layer", or "nickel-plating layer" + "a galvanization layer" on ** "a desperation plating layer", and by request Furthermore, to a ** "copper plating layer" formation process, subsequently to a ** "copper plating layer" top, may perform the process which forms "nickel-plating layer", "galvanization layer", or "nickel-plating layer" + "a galvanization layer", and Again to a ** "copper plating layer" formation process or a ** "nickel-plating layer" formation process, a "galvanization layer" formation process, or a "nickel-plating layer" + "galvanization layer" formation process furthermore, subsequently The process which forms a chromate film on ** "copper plating layer" or ** "nickel-plating layer", "galvanization layer", or "nickel-plating layer" + "a galvanization layer" may be performed. The conditions like these additional processing should just follow it of a well-known approach.

[0025] In addition, the processed copper foil in the manufacture approach of this invention may be electrolytic copper foil, and may be rolling copper foil. By the approach of this invention, it is because the class of copper foil is not chosen.

[0026]

[Embodiment of the Invention] Below, this invention is explained in more detail based on an example. However, this invention is not limited to these.

[0027] Example 1(1) processed copper foil (original copper foil)

Electrolytic copper foil (granularity of a mat side: thickness: unsettled copper foil; 18 micrometers; Ra= 0.6 micrometers; Rz= 4.2 micrometers; product made from Koga Circuit Foil)

(2) Cathode electrolysis processing by direct current was performed to the formation Hara copper foil of a desperation plating layer on the following conditions, and electrocrystallization of the "desperation plating layer" which consists of a detailed projection group on the mat side of this original copper foil was carried out.

** A presentation and copper sulfate of the electrolytic solution : 100 g-CuSO₄, 5H₂ O/l, and a sulfuric acid 120 g-H₂SO₄/l and molybdenum : 0.6 g-Na₂MoO₄.2H₂ O/l and iron : 15g-FeSO₄.7H₂O/l** Temperature of the electrolytic solution: 35 degree-C** current density : 40 A/dm² ** processing time : Cathode electrolysis processing by direct current is performed to the aforementioned original copper foil by which the detailed projection group was formed on the 3.5sec.(3) capsule plating mat side on the following conditions. this -- the detailed projection group was covered by the copper thin layer.

** A presentation and copper sulfate of the electrolytic solution : 250 g-CuSO₄, 5H₂ O/l, and sulfuric acid : Temperature of the 100 g-H₂SO₄/l** electrolytic solution: 50 degree-C** current density : 20 A/dm² ** processing time : The further aforementioned processing of 7.0sec.(4) (2) -> (3) was repeated once again.

(5) the sample (henceforth "surface treatment copper foil") which gave nickel-Lynn plating (0.1 mg/dm²) and a galvanization (0.1 mg/dm²) to the front face by the side of the plane of composition-ed of surface treatment profit **** copper foil (henceforth "roughening processing copper foil"), and performed chromate treatment to it on it further was created.

[0028] The property of the obtained surface treatment copper foil was evaluated about the following item, respectively.

[0029] (1) Peel -- ***** -- having had -- what pressed surface treatment copper foil in FR-4 base material, and was pasted up -- a sample -- carrying out -- JIS C 6481 According to 5.7 of "the copper-clad laminate test method for printed wired boards", ordinary state Peel ("peel strength" in an ordinary state) was measured.

[0030] (2) Make into a sample what etched this surface-preparation copper foil into 1mm width of face after pressing hydrochloric-acid-proof degradation ***** surface-preparation copper foil in FR-4 base material and pasting up, follow 5.7 of JIS "the copper-clad laminate test method for printed wired boards", and they are ordinary state Peel and Peel after degradation processing (it is "peel strength" although this sample was immersed in the 25-degree C processing liquid which carried out tales-doses mixing of a hydrochloric acid and distilled water 35% for 1 hour.). C 6481 the following and "Peel after degradation" -- saying -- it measured and asked by count according to the following formula.

rate (%) of hydrochloric-acid-proof degradation =(1- (after [degradation] Peel / ordinary state Peel)) x - 100 [0031] (3) the test paper (Oriental filter paper No.2) was placed on powder omission profit **** surface treatment copper foil, and this test paper was dragged to 150mm horizontal direction, applying a load (250g/20mmphi) to it. Visual observation of the copper powder adhering to this test paper was carried out, and evaluation attachment was carried out at the order of A<B<C<D<E<F according to coating weight (A: powder omission "zero", F: there is most powder omission).

[0032] A result is shown in Table 1.

[0033] Except for having replaced the presentation of the electrolytic solution in example 2 processing (2) with the following, roughening processing copper foil and surface treatment copper foil were produced like the example 1, respectively, and the same characterization as an example 1 was performed about this surface treatment copper foil. A result is shown in Table 1.

** A presentation and copper sulfate of the electrolytic solution : 100 g-CuSO₄, 5H₂ O/l, and sulfuric acid : 120 g-H₂SO₄/l and molybdenum : 0.05 g-Na₂MoO₄.2H₂ O/l and a tungsten: 0.05 g-Na₂WO₄.2H₂ O/l [0034] Except for having replaced the presentation of the electrolytic solution in example 3 processing (2) with the following, roughening processing copper foil and surface treatment copper foil were produced like the example 1, respectively, and the same characterization as an example 1 was performed about this surface treatment copper foil. A result is shown in Table 1.

** A presentation and copper sulfate of the electrolytic solution : 100 g-CuSO₄, 5H₂ O/l, and sulfuric

acid : 120 g-H₂SO₄/l and molybdenum : 0.6 g-Na₂MoO₄.2H₂O/l and iron : 15 g-FeSO₄.7H₂O/l and tungsten: 0.03 g-Na₂WO₄.2H₂O/l [0035] Except for having replaced the presentation of the electrolytic solution in example 4 processing (2) with the following, roughening processing copper foil and surface treatment copper foil were produced like the example 1, respectively, and the same characterization as an example 1 was performed about this surface treatment copper foil. A result is shown in Table 1.

** A presentation and copper sulfate of the electrolytic solution : 100 g-CuSO₄, 5H₂O/l, and sulfuric acid : 120 g-H₂SO₄/l and molybdenum: 0.6 g-Na₂MoO₄.2H₂O/l and cobalt : 10 g-CoSO₄.7H₂O/l [0036] Except for having replaced the presentation of the electrolytic solution in example 5 processing (2) with the following, roughening processing copper foil and surface treatment copper foil were produced like the example 1, respectively, and the same characterization as an example 1 was performed about this surface treatment copper foil. A result is shown in Table 1.

** A presentation and copper sulfate of the electrolytic solution : 100 g-CuSO₄, 5H₂O/l, and sulfuric acid : 120 g-H₂SO₄/l and molybdenum: 0.6 g-Na₂MoO₄.2H₂O/l and nickel : 10 g-NiSO₄.7H₂O/l [0037] Except for having replaced the presentation of the electrolytic solution in example of comparison 1 processing (2) with the following, roughening processing copper foil and surface treatment copper foil were produced like the example 1, respectively, and the same characterization as an example 1 was performed about this surface treatment copper foil. A result is shown in Table 1.

** A presentation and copper sulfate of the electrolytic solution : 100 g-CuSO₄, 5H₂O/l, and sulfuric acid : 120 g-H₂SO₄/l and arsenic : 0.4 cc/l as 60% H₃AsO₄ (specific gravity: 1.58) [0038] Except for having replaced the presentation of the electrolytic solution in example of comparison 2 processing (2) with the following, roughening processing copper foil and surface treatment copper foil were produced like the example 1, respectively, and the same characterization as an example 1 was performed about this surface treatment copper foil. A result is shown in Table 1.

** A presentation and copper sulfate of the electrolytic solution : 100 g-CuSO₄, 5H₂O/l, and sulfuric acid : 120 g-H₂SO₄/l and molybdenum: 0.6 g-Na₂MoO₄.2H₂O/l [0039] the field which performed roughening processing of each roughening processing copper foil obtained in examples 1-5 and the examples 1-2 of a comparison -- the software etching reagent (g/l H₂SO₄: 100 --) of a sulfuric-acid-hydrogen peroxide H₂O₂ : It is immersed in 30 g/l and n-propanol:10 cc/l for 1 minute, and this roughening processing coat is dissolved. After carrying out decomposition removal of the hydrogen peroxide which carries out evaporation to dryness of this solution, and is contained in this solution, quantitative analysis of the object element in this solution was carried out in atomic absorption analysis (a Hitachi Z-6100 form polarization Zeeman atomic absorption spectro-photometer is used). The result is shown in Table 2. In addition, data are converted into the abundance in this roughening processing coat.

[0040]

[Table 1]

表 1

	やけめつき層中含 有金属 ^{*1}	ピール強 度 ^{*2} (kg/cm)	耐塩酸劣 化率 ^{*3} (%)	粉落ち ^{*4}
実施例 1	Mo, Fe	1.42	0	A
実施例 2	Mo, W	1.46	0	A
実施例 3	Mo, Fe, W	1.46	0	A
実施例 4	Mo, Co	1.43	2	C
実施例 5	Mo, Ni	1.42	2	C
比較例 1	As	1.46	0	B
比較例 2	Mo	1.28	2	E

〔備考〕

*1 銅を除く。

*2 常態ピールである。

*3 劣化率 = (1 - (常態ピール/劣化後ピール)) × 100

*4 目視観察結果である。

[0041]

[Table 2]

表 2

	表面処理被膜中の存在量 (mg/dm ²)					
	Mo	Fe	Co	Ni	W	As
実施例 1	0.020	0.006	-	-	-	-
実施例 2	0.002	-	-	-	0.002	-
実施例 3	0.013	0.002	-	-	0.001	-
実施例 4	0.011	-	0.002	-	-	-
実施例 5	0.008	-	-	0.002	-	-
比較例 1	-	-	-	-	-	0.172
比較例 2	0.021	-	-	-	-	-

〔備考〕 分析された元素は主体としての銅を除くものである。

[0042]

[Effect of the Invention] The copper foil of this invention has the engine performance which is not inferiority with that (one of the conventional techniques) for which the Peel reinforcement, the rate of hydrochloric-acid-proof degradation, and powder omission used the strong toxic arsenic as shown in Table 1. on the other hand, the molybdenum mentioned as other examples (poison is not included) of the conventional technique -- single -- it turns out that the copper foil of business has the low Peel reinforcement, and the problem of powder omission is also large many practically. That is, if this invention is followed, the environment-friendly copper foil with which it is fully satisfied of the

predetermined engine performance as copper foil for printed wired boards, and the manufacture approach for it can be offered.

[Translation done.]